Giant attosecond fluctuations of local optical fields in disordered nanostructured media

Mark I. Stockman*
Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303
(Received 27 June 2000)

We predict that local optical fields in disordered nanostructured systems (clusters, composites, and rough surfaces) experience giant fluctuations (chaotic changes similar to turbulence) at an *attosecond* temporal and nanometer spatial scale. These fluctuations are most pronounced for a femtosecond-pulse excitation. This predicted effect is especially important for ultrafast nonlinear phenomena.

We have recently witnessed phenomenal progress in the physics of ultrafast (femtosecond) phenomena[1–11] (see also references therein). Ultraintense laser pulses, with intensity up to 10^{20} W/cm^2, have been generated whose interaction with matter induces a wide range of deeply nonlinear effects. These effects comprise the generation of high harmonics from the visible to x-ray region,[1] strong x-ray emission from hot plasmas produced by irradiation of colloidal metals and grooved surfaces,[5] nanostructured ''velvet'' targets,[11] clusters in gases,[6] and preformed high-density plasmas.[8] Multiple photoionization of metal clusters enhanced by plasmons[7] has been produced. Photonuclear reactions and the emission of γ radiation and high-energy electrons have been discovered[9,10] induced by a solid-target excitation by femtosecond pulses with intensities $10^{19}-10^{20}$ W/cm^2.

The interaction of ultraintense light pulses with disordered nanostructured systems (clusters, composites, and rough surfaces) is highly efficient[5] due to two fundamental reasons. First, many such systems provide a strong radiation-matter coupling, thus facilitating the accumulation of the electromagnetic energy in the matter. Second, the local (acting) fields can be greatly enhanced with respect to the exciting laser fields. Such enhancement has been earlier theoretically predicted[12–14] for the steady-state excitation for a wide class of random nanostructured systems with both conventional and fractal geometries and directly observed experimentally (see, e.g., Refs. 15 and 16 and citations therein).

Recently we have predicted[17] an effect (called ''the ninth wave'' effect) for ultrafast optical excitation. It consists of a transient (femtosecond) generation of regions of very high local fields, which occurs when the duration of an exciting pulse T is longer than the optical period T_0 but much shorter than the dissipation (T_1) time (this condition is realistic for a variety of systems), causing accumulation of the excitation energy in the system. At the same time, the giant fluctuations of local optical fields[13] set in, because that requires only a comparatively short period, on the order of the establishment time of the eigenmodes of the system, i.e., time $t \gtrsim T_0$. These fluctuations lead to a concentration of the conserving excitation energy of the entire extended system in small spatial regions on the time scale $t \simeq T$ (typically, from several to tens of femtoseconds).[17]

In this paper we predict an effect that is one of the fastest phenomena possible in optics. We show that in disordered nanostructured systems the spatial distribution of the local optical fields changes dramatically and chaotically (resembling developed turbulence) on an *attosecond* temporal scale (*within* the optical period) and on a nanometer spatial scale. The underlying physical cause of these attosecond-nanometer giant fluctuations is chaos of the polar eigenmodes of the system that leads to random magnitudes and phases of the local fields in the vicinity of different particles (monomers) of the system.[14] At the same time, the correlation function of the local fields extends over the whole system due to the infinite range of the dipole interaction.[14] Because a wave moves in the direction of its increasing phase, the evolution of the light-induced polar wave (local fields) does not resemble an ordered wavelike oscillation, but rather excitation moves chaotically in space over the entire extent of the system following its random phase. This predicted effect is linear, similar to quantum chaos in this respect. However, it will strongly influence a variety of nonlinear effects, such as the generation of high harmonics, ionization, and laser-induced nuclear reactions mentioned above.

To quantitatively introduce the present effect, we consider a system consisting of $N \gg 1$ polarizable particles (monomers) positioned at coordinates $\mathbf{r}_i$, $i=1,\ldots,N$. We employ the retarded Green's function $G^r_{i\beta,j\gamma}(t-t')$ that expresses the local field $\mathbf{E}_i(t)$ at an ith monomer at time t in terms of the exciting (external) field $\mathbf{E}^{(0)}_j(t')$ at the jth monomer at a moment t',

$$E_{i\beta}(t)=\sum_{j=1}^{N}\int_{-\infty}^{t} G^r_{i\beta,j\gamma}(t-t')E^{(0)}_{j\gamma}(t')dt'. \qquad (1)$$

Here and below, Greek subscripts denote Cartesian components with summation over recurring indices implied.

We define a local field $\mathbf{E}_i$ in terms of the corresponding induced dipole moment $\mathbf{d}_i(\omega)=\alpha_0(\omega)\mathbf{E}_i(\omega)$, where $\alpha_0(\omega)$ is the dipole polarizability of an isolated monomer at a frequency ω. Throughout the paper, we imply the Fourier (frequency) domain by indicating frequency argument ω, as opposed to time variables $t,t',\ldots$ for the real-time domain. In specific computations, we consider the monomers as spheres of radius R_m, for which $\alpha_0(\omega)=R_m^3[\epsilon(\omega)-1]/[\epsilon(\omega)+2]$, where $\epsilon(\omega)$ is the relative dielectric function of the monomer material.

To concentrate on the essence of this effect and avoid unnecessary complications, we assume that the total size of the system R is small compared to the radiation wavelength, $R \ll cT_0$, which makes the electromagnetic retardation unim-

portant. This is justified because the dynamics of interest occurs on a nanometer scale where the dipole modes of the system (''surface plasmons'') are localized.[12,14] At the same time, the spatial scale of energy transfer is the correlation radius of the eigenmodes that is of the order of the size of the system,[12,14] $R \gg R_m$. This allows us to use the dipole approximation and techniques of dipole spectral expansion.[18] A generalization for the case of multipole interactions and exact spectral expansion[19] will be described elsewhere.

The retarded Green's function in the frequency domain has a spectral expansion[17]

$$G^r_{i\beta,j\gamma}(\omega)=\sum_n (i\beta|n)(j\gamma|n)[1+\alpha_0(\omega)W_n]^{-1}. \quad (2)$$

Here $|n)$ and W_n are eigenvectors (eigenmodes) and eigenvalues of the dipole-interaction operator W, $(W-W_n)|n)=0$, where $n=1,\ldots,3N$ is the eigenmode's descriptor, and $(i\beta|W|j\gamma)=-(\partial/\partial r_{i\beta})(\partial/\partial r'_{j\gamma})(1/|\mathbf{r}_i-\mathbf{r}'_j|)$. Each eigenvalue W_n and amplitude $(i\beta|n)$ of an nth eigenmode at an ith monomer with polarization β are computed by a numerical diagonalization of W.

We have carried out our numerical computations using Eqs. (1) and (2) without simplifications other than stated above. However, to provide qualitative insight into properties of the proposed effect, we consider an approximation of small optical absorption, $\Delta(\omega)\ll|X(\omega)|$, where the spectral parameters have standard definitions:[18] $X(\omega)\equiv-\mathrm{Re}Z(\omega)$ and $\Delta(\omega)\equiv-\mathrm{Im}Z(\omega)$, where $Z(\omega)\equiv 1/\alpha_0(\omega)$. In this approximation, the Green's function in the time domain can be found in the form

$$G^r_{i\beta,j\gamma}(t)=\delta_{ij}\delta_{\beta\gamma}\delta(t) + 2\theta(t)\int S_{i\beta,j\gamma}(\omega)\beta(\omega)\sin(\omega t)e^{-\gamma(\omega)t}d\omega, \quad (3)$$

where the autocorrelation function of the eigenmode amplitudes[14] in the site-frequency representation is

$$S_{i\beta,j\gamma}(\omega)=\sum_n (i\beta|n)(j\gamma|n)\delta(\omega-\omega_n). \quad (4)$$

In Eqs. (3) and (4), $\beta(\omega)\equiv X(\omega)/[dX(\omega)/d\omega]$, $\gamma(\omega)\equiv\Delta(\omega)/[dX(\omega)/d\omega]$, and ω_n is an eigenfrequency given by the root of the equation $X(\omega_n)=W_n$. The summation in Eq. (4) should be extended over all roots for which $\Delta\ll|X|$. Such roots correspond to normal dispersion, and $\gamma(\omega_n)>0$ automatically for them. The Green's function (3) is asymptotically exact for $t\gg 1/\omega_n$.

Dynamics determined by Eq. (3) is multiexponential with dissipation times $\tau_d(\omega_n)=1/\gamma(\omega_n)$. For instance, for silver in the visible region $\tau_d=40-120$ fs. Consider a short exciting pulse whose duration $T\lesssim\tau_d$ renders dissipation ineffective. The local fields according to Eqs. (1), (3), and (4) are formed by a superposition of interfering ''waves'' $(j\gamma|n)\sin(\omega_n t)$ that are chaotic.[14] Given the wide spectral contour of the system, the range of eigenfrequencies that contributes to that superposition is $\Delta\omega_n\simeq 1/T$, which leads to phase differences at a time t of $\Delta\varphi\simeq t\Delta\omega_n\simeq t/T$. The maximum excitation concentration and the highest local field (the ninth wave) are reached at time $t\simeq T$.[17] Together with the randomness of eigenfrequencies ω_n, this implies that at the moment of the ninth wave the phases of interfering waves are random in the whole range from 0 to 2π. This and the chaotic behavior[14] of the correlation function (4) leads to *random phases* of local fields *in space*. This creates a chaotic spatial distribution of local fields changing *within the optical period, i.e., at attosecond times* and on a nanometer spatial scale.

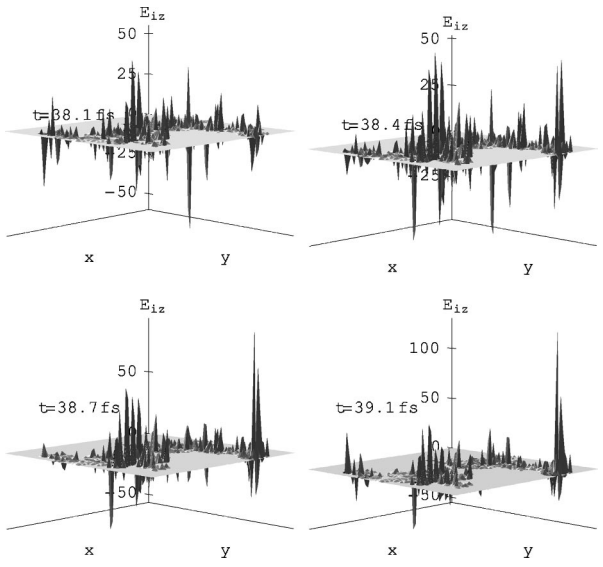

FIG. 1. Local fields $E_{iz}(t)$ for a 3D CCA cluster as functions of the spatial coordinates (x,y) for the moments of time indicated in the figure for an exciting pulse of $T=25$ fs length, carrier frequency $\omega_0=1$ eV, and linear z polarization. The time interval between frames is ≈ 300 as. The distance in space between neighboring monomers is on a nanometers scale. The fields are summed over z for all monomers with the same (x,y) to display the required 3D distribution on a planar figure.

We have performed numerical calculations using Eqs. (1) and (2) for three types of disordered nanostructured systems built of nanospheres as monomers. These are cluster-cluster aggregate (CCA) clusters[20,21] in three dimensions (3D) and two dimensions (2D) (fractals with Hausdorff dimensions $D\approx 1.75$ and $D\approx 1.4$), and random suspensions of monomers in a host (Maxwell Garnett composites) with the fill factor $f=0.12$ and the periodic boundary conditions at the unit cell. The number of monomers in a cluster or in the unit cell of the composite is $N=1500$, and the dielectric properties of the monomer material are set to be those of bulk silver.[22] The host medium is vacuum for clusters and a dielectric with constant $\epsilon_h=2.0$ for composites. The exciting pulse is chosen in the Gaussian form with a unit amplitude, carrier frequency ω_0, and duration T, $E^{(0)}(t)=\cos(\omega_0 t)\exp(-t^2/T^2)$. For each system, ω_0 has been chosen near the absorption maximum. The dielectric function $\epsilon(\omega)$ is known in the interval of $\Delta\omega\simeq 7$ eV that is much wider than the required spectral width greater or on the order of that of the exciting pulse $\Delta\omega_n\simeq 0.1$ eV. This allows one to correctly describe the temporal dynamics.

The predicted effect of giant attosecond fluctuations is illustrated in Fig. 1 that shows the dynamics of local fields for a 3D CCA cluster excited by a 25-fs pulse. This figure consists of four frames showing instantaneous spatial distri-

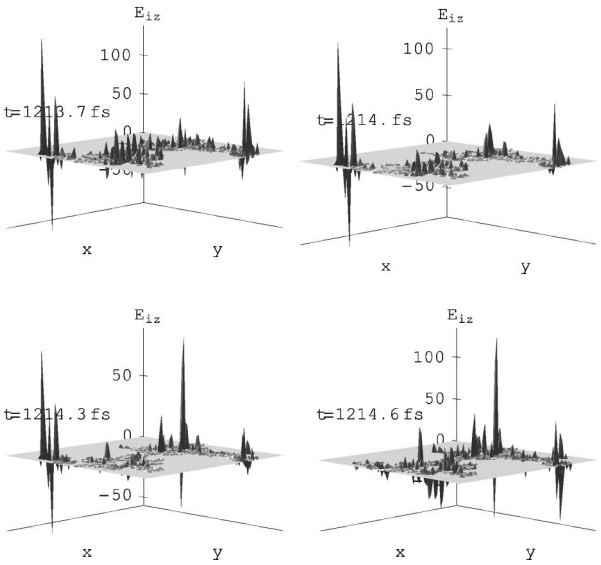

FIG. 2. Similar to Fig. 1 but for pulse length $T=1$ ps.

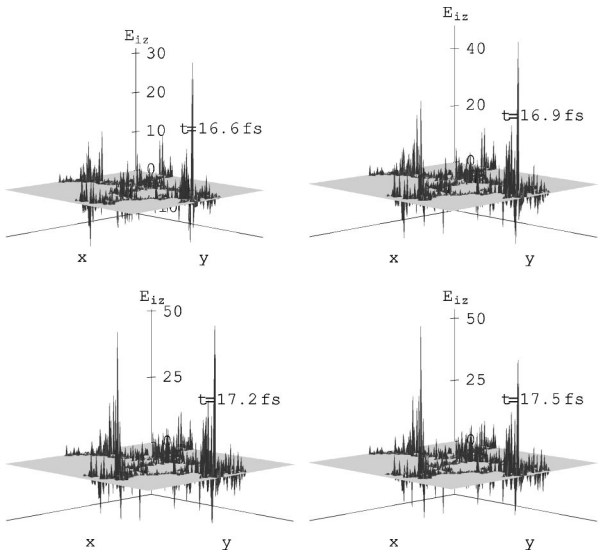

FIG. 3. Similar to Fig. 1, but for 2D CCA clusters. The pulse length is 15 fs and the carrier frequency is $\omega_0=1.2$ eV.

butions of local fields. The frames are separated by ≈ 300 as time intervals ending by the moment of the global maximum of the fields (the ninth wave) at $t=39.1$ fs after the pulse beginning. The total time span shown is a quarter of the light period (≈ 1 fs). The most important property of this figure is dramatic changes of the spatial distribution between the frames *at attosecond temporal and nanometer spatial scales* that bear qualitative signatures of spatio-temporal chaos. At each moment in time, these spatial distributions are highly random and singular as expected for the giant fluctuations, with a significant enhancement in peaks (''hot spots'') with respect to the exciting field. For the ninth wave, this enhancement exceeds two orders of magnitude (cf. Ref. 17). The evolution shown is due to the chaotic evolution of a packet of ''waves'' of eigenmodes with random magnitudes and phases, as suggested above, and not a harmonic oscillation of the type of a standing wave or running wave, which may be expected for an ordered system.

The argument of a chaotic local-field wave that follows the random phase at different monomers generating an attosecond-nanometer chaotic dynamics due to the underlying chaos of eigenmodes is applicable not only to ultrafast (nondissipative) femtosecond excitation but also (in a modified form) to a steady-state ($T\rightarrow\infty$) excitation. This circumstance has been completely overlooked before. In the steady-state case, the local fields

$$E_{i\beta}(t)=\mathrm{Re}\sum_j\,[G^r_{i\beta,j\gamma}(\omega_0)e^{-i\omega_0 t}E^{(0)}_{j\gamma}] \tag{5}$$

are formed with the participation of the dissipation [described by parameter $\Delta(\omega)$]. Their magnitudes and phases are also chaotic,[14] but completely different from those for femtosecond excitation. In Fig. 2 we present the predicted spatio-temporal dynamics for a quasistationary excitation ($T=1$ ps$\gg\tau_d$). Giant nanometer-attosecond scale fluctuations are evident, as well as a dramatic difference from Fig. 1 above.

The predicted effect is based on an idea of giant fluctuations,[13] a general property of self-similar (fractal) systems with the long-range (dipole) interaction. Therefore, it should be universally observable for fractal clusters irrespectively of their topology, Hausdorff dimension D, or the dimension of the embedding space d. To demonstrate this, in Fig. 3 we present data for an ultrashort ($T=15$ fs) exciting pulse for a 2D CCA cluster ($D\approx 1.4$ and $d=2$) that simulate roughness of surfaces. This figure does exhibit an attosecond-nanometer dynamics that is indeed chaotic with the same qualitative features as for 3D CCA (cf. Fig. 1). These include a significant enhancement in the leading peaks of a local field that reaches the maximum at the moment of the ninth wave ($t=17.5$ fs into the pulse). A completely different attosecond-nanometer dynamics shown in Fig. 4 takes place for a quasistationary pulse ($T=1$ ps). These data confirm that the effect of attosecond giant fluctuations is common for self-similar systems for both conditions of ultrashort and steady-state excitation. However, the specific dynamics is completely different in those two cases.

To investigate whether fractality is crucial or if disorder alone would suffice for the giant attosecond fluctuations, we

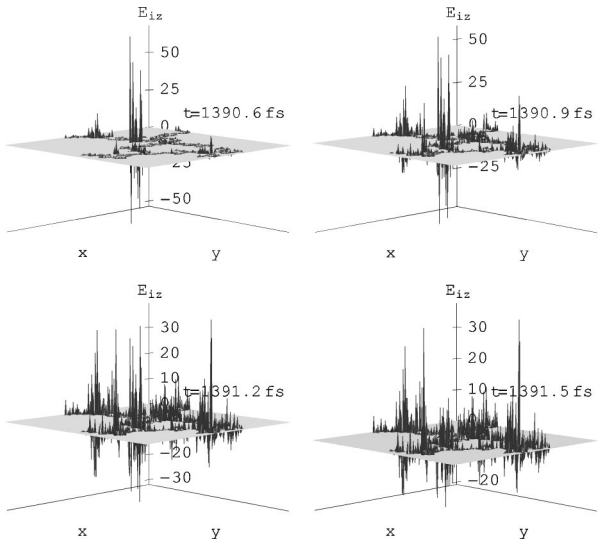

FIG. 4. Similar to Fig. 3 but for pulse length $T=1$ ps.

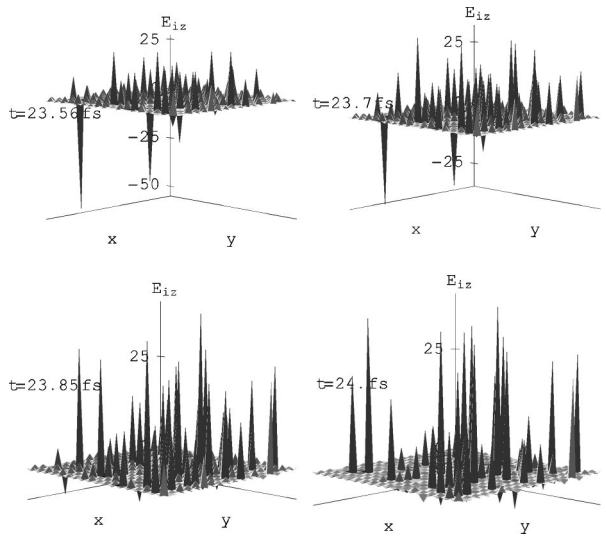

FIG. 5. Similar to Fig. 1 but for a Maxwell Garnett composite of silver nanospheres. The pulse length is $T=15$ fs and the carrier frequency is $\omega_0=2.5$ eV. The frames shown are separated by time intervals of ≈ 140 as.

consider a Maxwell-Garnett nanocomposite, i.e., a (nonfractal) random suspension of silver nanospheres in a dielectric host. The local fields excited by a 15-fs pulse are shown in Fig. 5. In this case, we also observe the attosecond-nanometer chaotic dynamics. However, in contrast to fractals, a significant concentration of the excitation energy in a narrow spatial region never happens. Instead, there is an average density of peaks of local fields on the same order of magnitude. This is due to the existence of the thermodynamic limit (characterized with finite densities) for nonfractal systems. A qualitatively similar, but quantitatively completely different attosecond-nanometer dynamics occurs during a quasistationary excitation ($T\rightarrow\infty$) (data not shown), analogously to the situation with fractals.

To briefly summarize the results obtained, we have predicted an effect of attosecond-nanometer giant fluctuations of local optical fields in disordered nanostructured systems. This effect is a general property based on chaoticity of the eigenmodes in such systems and is most pronounced for an ultrafast (femtosecond) excitation, although it also exists for a steady-state excitation. The effect manifests itself as chaotic (similar to turbulence) changes of local optical fields in time on the attosecond scale (i.e., within the optical period) and in space on the nanometer scale (i.e., within the wavelength). Though at the present time it is impossible to directly measure attosecond local-field dynamics, this possibility may appear in the future due to dramatic progress in the field. The attosecond giant fluctuations will also manifest themselves in a broad range of ultrafast optical phenomena, especially such highly nonlinear phenomena as laser-induced generation of energetic electrons, ions, x-rays, and nuclear reaction products from the attosecond ''hot spots.'' These emissions are much more enhanced than they would have been without the contribution of the effect of giant attosecond fluctuations. Based on its expected universality, this effect should be observable for a wide class of random nanostructured systems.

I am grateful to S. Manson for useful comments.

*Email: mstockman@gsu.edu; Web site: www.phy-astr.gsu.edu/stockman

[1] Z. Chang, R. Rundquist, H. Wang, M. Murnane, and H. C. Kapteyn, Phys. Rev. Lett. **79**, 2967 (1997).
[2] S. Backus, C. G. Durfee, M. M. Murnane, and H. C. Kapteyn, Rev. Sci. Instrum. **69**, 1207 (1998).
[3] I. P. Christov, M. M. Murnane, and H. C. Kapteyn, Phys. Rev. Lett. **78**, 1251 (1997).
[4] F. L. Kien, K. Midorikawa, and A. Suda, Phys. Rev. A **58**, 3311 (1998).
[5] M. M. Murnane, H. C. Kapteyn, S. P. Gordon, J. Bokor, E. N. Glytsis, and R. W. Falcone, Appl. Phys. Lett. **62**, 1068 (1993).
[6] T. Ditmire, T. Donnelly, R. W. Falcone, and M. D. Perry, Phys. Rev. Lett. **75**, 3122 (1995).
[7] L. Köller, M. Schumacher, J. Köhn, J. Tiggesbaumker, and K. H. Meiwes-Broer, Phys. Rev. Lett. **82**, 3783 (1999).
[8] R. Kodama, K. A. Tanaka, Y. Sentoku, T. Matsushita, K. Takahasi, H. Fujita, Y. Kitagawa, Y. Kato, T. Yamanaka, and K. Mima, Phys. Rev. Lett. **84**, 674 (2000).
[9] K. W. D. Ledingham *et al.*, Phys. Rev. Lett. **84**, 899 (2000).
[10] T. E. Cowan *et al.*, Phys. Rev. Lett. **84**, 903 (2000).
[11] G. Kulcsár, D. AlMawlawi, F. W. Budnik, P. R. Herman, M. Moskovits, L. Zhao, and R. S. Marjoribanks, Phys. Rev. Lett. **84**, 5149 (2000).
[12] M. I. Stockman, L. N. Pandey, and T. F. George, Phys. Rev. B **53**, 2183 (1996).
[13] M. I. Stockman, L. N. Pandey, L. S. Muratov, and T. F. George, Phys. Rev. Lett. **72**, 2486 (1994).
[14] M. I. Stockman, Phys. Rev. Lett. **79**, 4562 (1997); Phys. Rev. E **56**, 6494 (1997).
[15] P. Zhang, T. L. Haslett, C. Douketis, and M. Moskovits, Phys. Rev. B **57**, 15 513 (1998).
[16] S. I. Bozhevolnyi, V. A. Markel, V. Coello, W. Kim, and V. M. Shalaev, Phys. Rev. B **58**, 11 441 (1998).
[17] M. I. Stockman, Phys. Rev. Lett. **84**, 1011 (2000).
[18] V. A. Markel, L. S. Muratov, and M. I. Stockman, Zh. Éksp. Teor. Fiz. **98**, 819 (1990) [Sov. Phys. JETP **71**, 455 (1990)]; V. A. Markel *et al.*, Phys. Rev. B **43**, 8183 (1991).
[19] D. J. Bergman and D. Stroud, in *Properties of Macroscopically Inhomogeneous Media*, edited by H. Ehrenreich and D. Turnbull, Solid State Physics Vol. 46 (Academic Press, Boston, 1992), p. 148.
[20] P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983).
[21] M. Kolb, R. Botet, and J. Julienne, Phys. Rev. Lett. **51**, 1123 (1983).
[22] P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).